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Thermal Decomposition of Ammonium per Chlorate – Tetra Methyl Ammonium Tetrafluoroborate Mixture: a Simultaneous TG-MS Approach

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ABSTRACT

The control of combustion processes in composite solid rocket propellants is of prime importance from the point of view of thrust variation. To attain a specific thrust-time pattern required for a particular mission, it necessitates altering or modifying the combustion rates of these composite solid rocket propellant motors. These modifications can be achieved by the addition of small percentage of suitable additives. Present work is focused on the study of thermal behavior of a mixture of ammonium per chlorate – tetramethyl ammonium tetrafluoroborate through a simultaneous TG-MS approach, in an inert atmosphere of pure nitrogen, at a sample heating rate of $10^{o}C.min^{-1}$, and at a gas flow rate of $30 ml.min^{-1}$. The mechanistic aspect of thermal decomposition of this mixture is discussed.

Keywords: Ammonium per chlorate, Tehra-n-butyl tetra fluoraborate, decomposition mixture.

1. INTRODUCTION

The control of combustion processes in composite solid rocket propellants is of prime importance from the point of view of thrust variation. To attain a specific thrust-time pattern required for a particular mission, it necessitates altering or modifying the combustion rates of these composite solid rocket propellant motors. These

modifications can be achieved by the addition of small percentage of suitable additives.

In the process of identifying suitable compounds for the suppression of the first exotherm of ammonium per chlorate, which was supposed to be responsible for the premature re-ignition of quenched composite solid propellant rocket motors, ammonium compounds such as NH_4BF_4 were studied[1]. Investigation of organic per chlorates such as methylamine per chlorate, dimethylamine per chlorate, and trimethylamine per chlorate was reported by Fogel'zang *et al*.[2]. Thermo analytical studies on Carboxyl terminated polybutadiene (CTPB) – Ammonium per chlorate composite solid rocket propellants employing NH_4BF_4 as an additive were reported by Prasad *et al*.[3].

In the present work, focus has been made towards understanding the role of tetramethyl ammonium tetrafluoroborate (TMATFB) in the modification of thermal decomposition behavior of ammonium per chlorate (AP).

2. EXPERIMENTAL

The TG – SDTA - MS experiments were conducted in a Mettler - 851e system, and DSC in Mettler 821e system; in an inert atmosphere of pure nitrogen, at a sample heating rate of $10^{o}C.min^{-1}$, and a gas flow rate of $30\ ml.min^{-1}$.

Pure ammonium per chlorate (AP) was procured from the Ammonium per chlorate experimental plant (APEP), Alwaye, Indian Space Research Organization, Department of Space, Government of India. Pure compound of tetramethyl ammonium tetrafluoroborate (TMATFB) was procured from M/s. Sigma Aldrich.

3. RESULTS AND DISCUSSION

The TG – DTG curves of pure ammonium per chlorate is shown in Fig.1. The onset of decomposition is at 277.1^{o}C. The first-stage decomposition peak appears at 301.2^{o}C. The second – stage decomposition peak (a minor peak) appears at 353.6^{o}c, and the major third-stage decomposition appears at 440^{o}C. The decomposition comes to an end at about 442.6^{o}C.

The TG – DTG curves of TMATFB is shown in Fig.2. The onset of decomposition of this compound is at 434.6^{o}C, while the end set temperature of decomposition is at 487.6^{o}C. The maximum rate of decomposition occurs at 474.2^{o}C. Compared to ammonium perchlorate, the tetramethyl substituted ammonium per chlorate is more thermally stable.

The TG – DTG curves of a mixture of AP – TMATFB with TMATFB concentration being 0.50 percent of AP is shown in Fig.3. The onset of decomposition is at 279.5^{o}C, and the end set of decomposition is at 448.3^{o}C.

The addition of 0.5 percent TMATFB has brought down the temperature of end set of decomposition by about 39^{o}C, indicating the catalytic activity by TMATFB. The peaks corresponding to the three steps of decomposition appear at 304.2^{o}C, 361.5^{o}C, and 437.7^{o}C, respectively. Apparently, it appears that TMATFB had a small influence on the second-stage decomposition of AP by shifting it towards higher temperature region by about 8^{o}C. Its effect on the onset and end set temperatures of decomposition of AP is minimal or negligible.

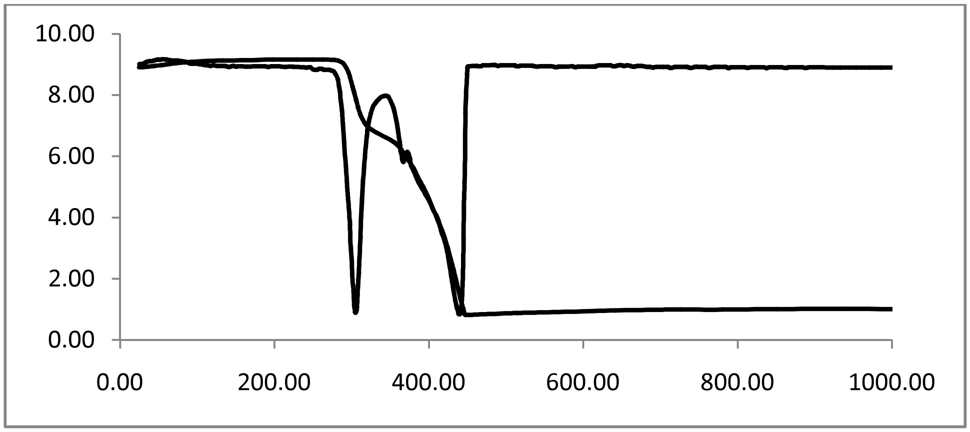

Fig.1. TG-DTG of Ammonium Per chlorate.

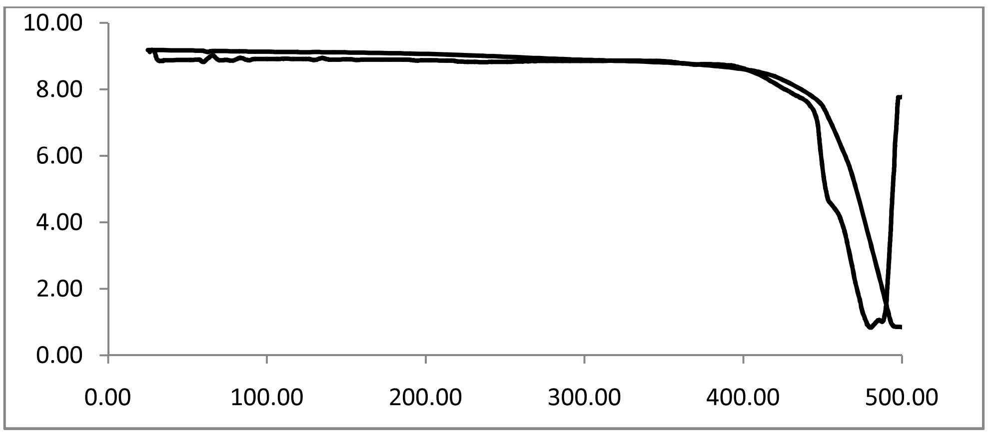

Fig.2. TG-DTG of Tetra methyl Ammonium Tetrafluoroborate.

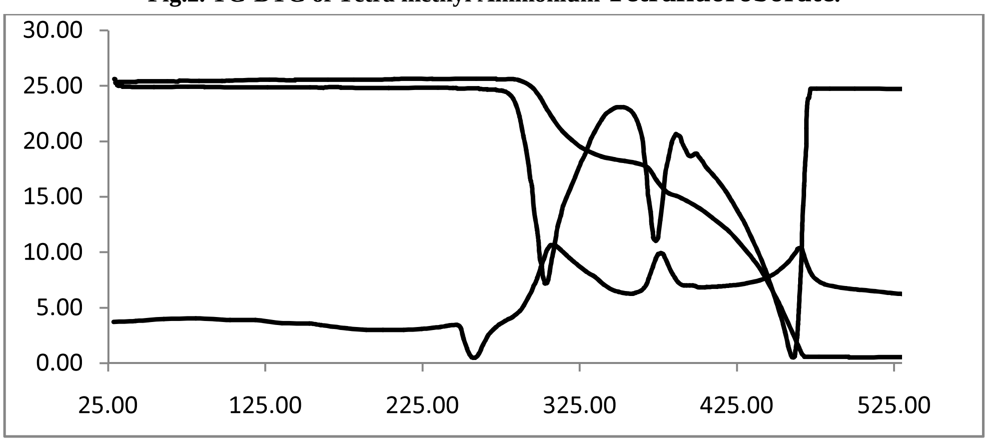

Fig.3. Simultaneous TG – DTG – DTA of AP – TMATFB Mixture

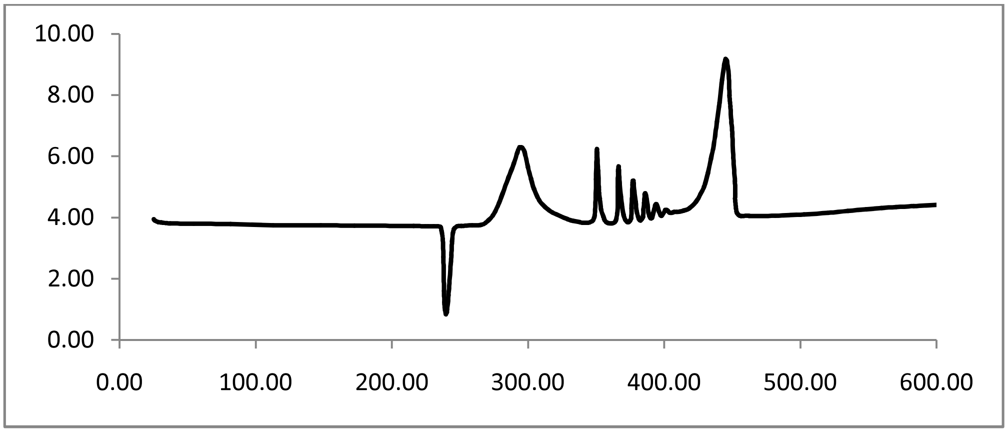

Fig.4. DSC Curve of Pure Ammonium Per chlorate

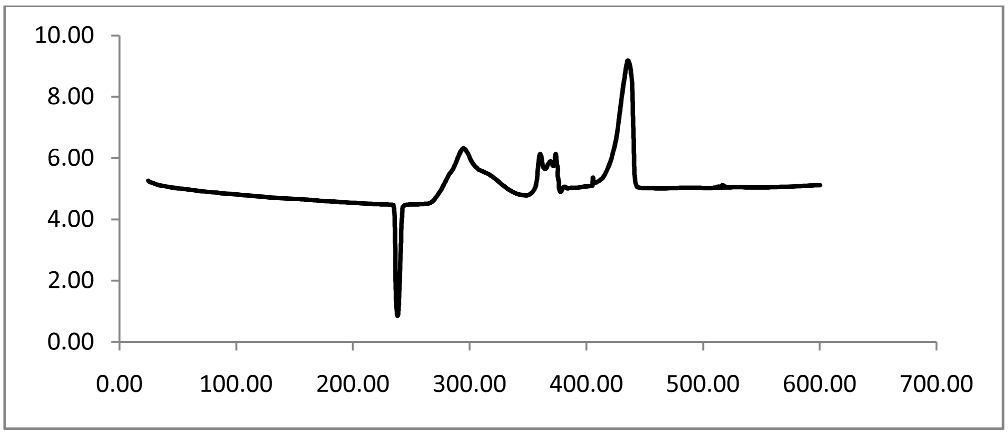

Fig.5. DSC Curve of AP + TMATFB Mixture

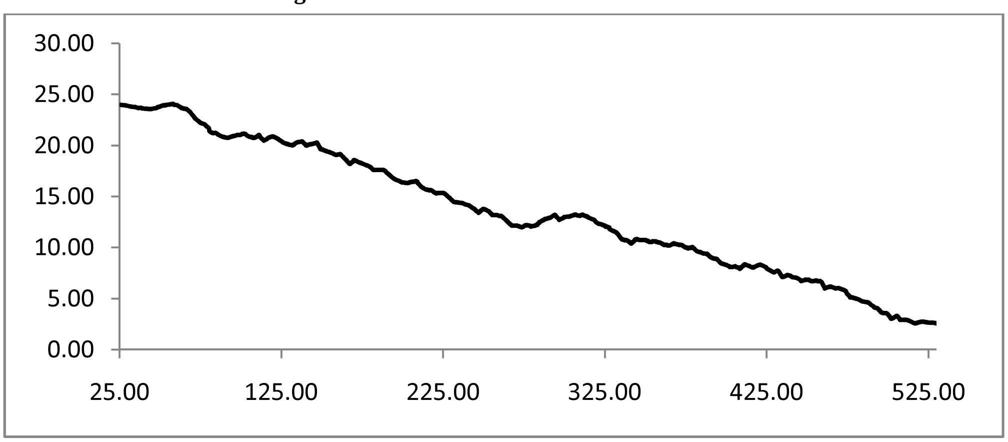

Fig.6. Evolution of mass fragment corresponding to m/z=11

The DSC – curves of pure AP and the mixture of AP with TMATFB are shown in Fig.4 and Fig.5. The overall enthalpy value for AP is 2079.2 $J.g^{-1}$ and the same for AP – TMATFB mixture is 824.1 $J.g^{-1}$. This suggests that, TMATFB is acting as the suppressant or inhibiting the decomposition of AP. Apparently, it seems that TMATFB can act as a suppressant for the first – stage decomposition of AP, as evident from the peak heights.

The evolution curves of mass fragments corresponding to m/z=11, 15, 16, 17, 19, 35, 49, 59, and 68 are shown through Fig.6 to Fig.14.

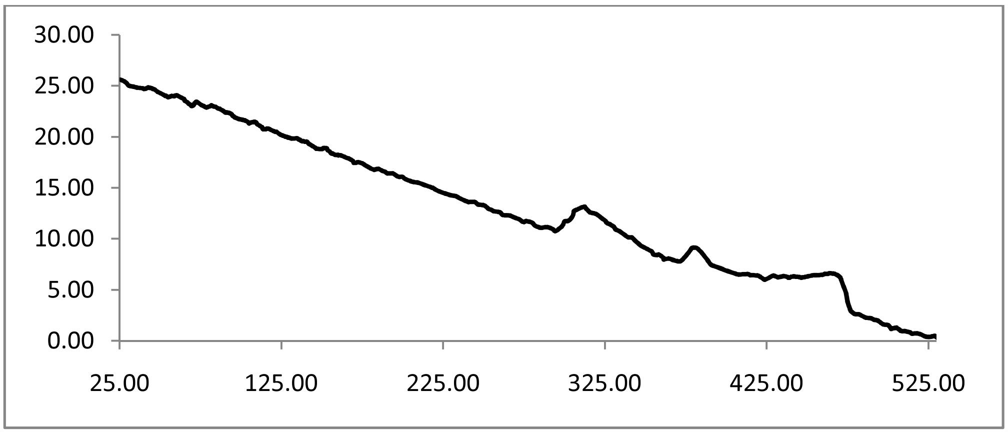

Fig.7. Evolution curve corresponding to mass fragment m/z=15

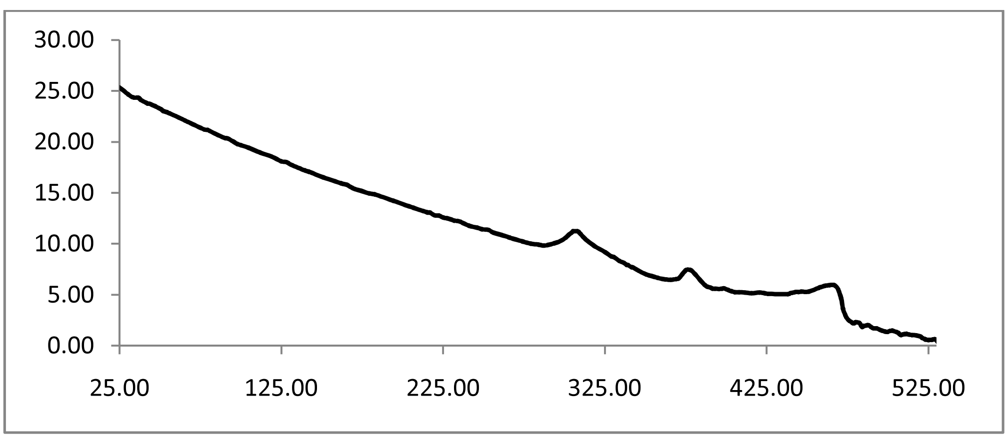

Fig.8. Evolution curve corresponding to mass fragment m/z=16

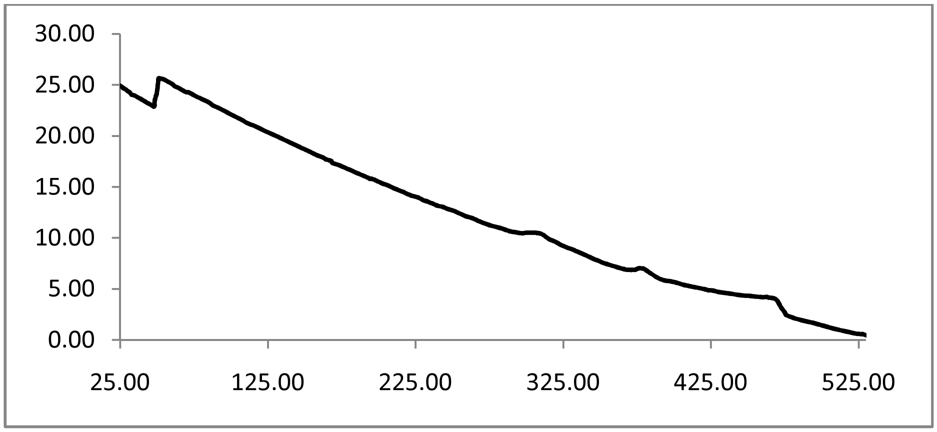

Fig.9. Evolution curve corresponding to mass fragment m/z=17

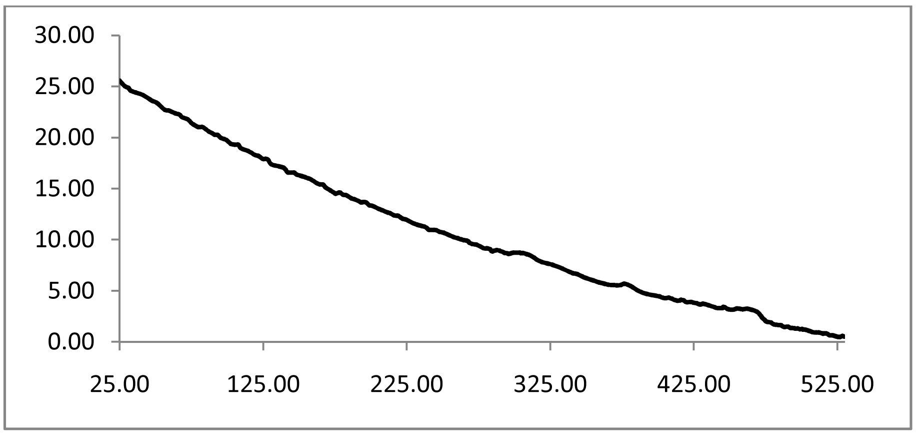

Fig.10. Evolution curve corresponding to mass fragment m/z=19

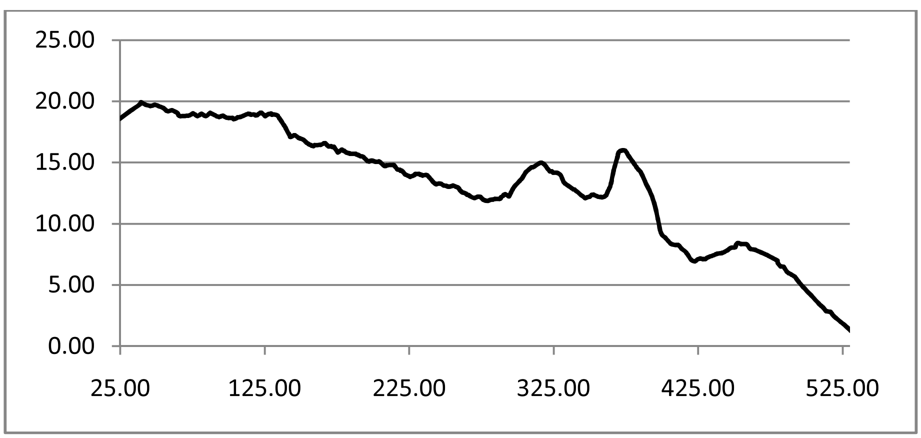

Fig.11. Evolution curve corresponding to mass fragment m/z=35

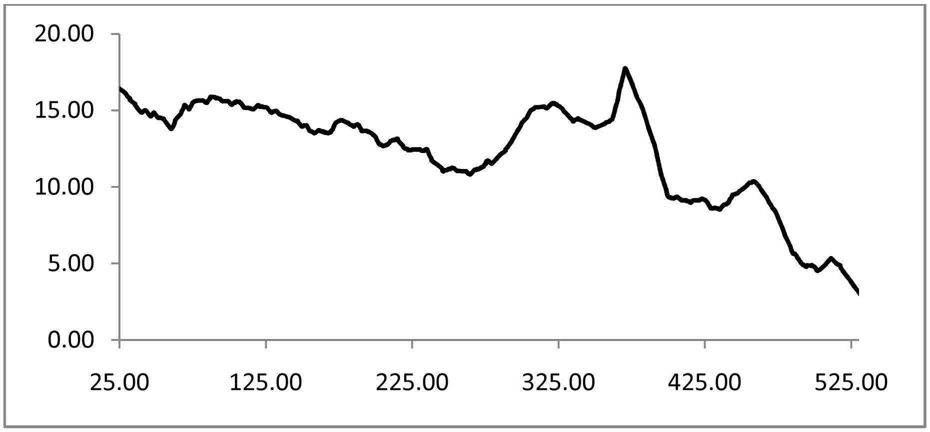

Fig.12. Evolution curve corresponding to mass fragment m/z=49

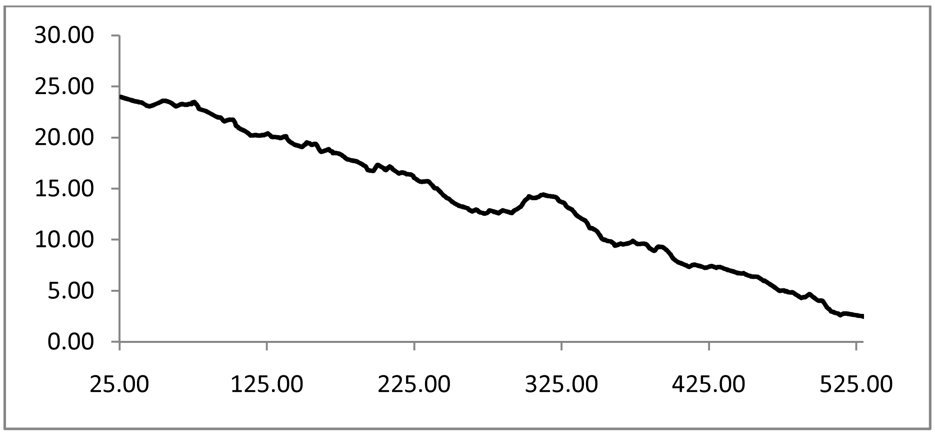

Fig.13. Evolution curve corresponding to mass fragment m/z=59

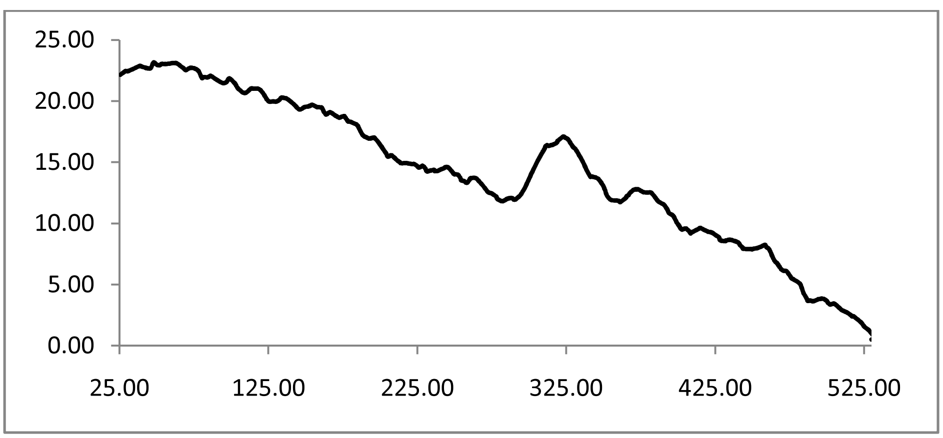

Fig.14. Evolution curve corresponding to mass fragment m/z=68

Ammonium tetrafluoroborate (AFB) is known to decompose giving NH_3, HF, and BF_3[1]. Tetra methyl ammonium tetrafluoroborate being analogous to AFB, can be expected to behave in a similar manner. Accordingly, the expected products of its decomposition could be – $(CH_3)_3N$, CH_3F, and BF_3. The appearance of a mass fragment corresponding to m/z=59 corresponds to the formation of $(CH_3)_3N$. The appearance of a mass fragment corresponding to m/z=68 corresponds to the formation of BF_3. The peak corresponding to m/z =35 could be due to the appearance of Cl^+, similar to the one observed in the case of methyl substituted ammonium per chlorates[4]. The evolution of fragments corresponding to m/z =11,15, 16,17,19 are attributed to the formation of transient species such as B^+, CH_3^+,O^+, OH^+/NH_3^+, and F^+. The molecular fragment corresponding to m/z=49 is a strong indication of the formation of BF_2. The formation of BF_2 was observed in the case of tetra-n-butyl ammonium tetrafluoroborate as well[5].

4. CONCLUSION

Bothe from the decomposition temperature consideration and enthalpy consideration in respect of AP and its mixture with TMATFB, it is evident that TMATFB is acting as suppressant. TMATFB seems to be a useful system for suppressing the first exotherm of AP which appears to be responsible for the premature re-ignition of controllable solid rocket motors.

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